

The Study of Layer-by-Layer Ultrathin Films by the Dynamic Contact Angle Method

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The self-assembly film fabricated via the layer-by-layer technique was studied by the dynamic contact angle (DCA) method (Wilhelmy plate method). The used polyelectrolytes are poly(diallyldimethylammonium chloride) (PDDA), poly(etheleneimine) (PEI), diphenylamine-4-diazonium-formaldehyde resin (DR), 2-nitro-*N*-methyl-4-diazonium-formaldehyde resin (NDR), and poly(sodium-*p*-styrenesulfonate) (PSS). For the self-assembly systems of PDDA/PSS, PEI/PSS, DR/PSS, and NDR/PSS, their individual contact angle fluctuates regularly with the fabrication of each layer, while the magnitude of different systems' contact angle depends on the participant polycation. The re-organization of components and the adjacent layer interpenetration are presented here to explain this phenomena. We also found that DR or NDR can adsorb itself via the layer-by-layer method to form multilayer film, and the hydrophobic interaction is put forward to effect this process. Moreover, the procedure of washing and drying after adsorption was studied and considered as a prerequisite for the successful fabrication, especially of the same charge carried components. © 2001 Academic Press

INTRODUCTION

It is well known that the layer-by-layer ultrathin film can be fabricated from oppositely charged polyelectrolytes. Since Decher and his co-workers (1, 2) first put forward this method named self-assembly in most of the references (3–8), it has widely developed in recent years in the applied varieties, which includes DNA (9), protein (10), charged particles (11–13), etc., the mechanism of the film's formation (14–16), and the inner structure (17–19). But generally, the factors that influence the film's formation are still not fully understood. Usually, the driving force of the film growth was thought to be relying on charge overcompensation of the newly adsorbed polyions, i.e., the complement of electrostatic attraction of the cation–anion pairs formed in successive adsorption steps (2). But the electrostatic attraction was considered, especially in the recent past, not a prerequisite since the multilayer film can be fabricated from same charge carried polymers (20).

To characterize this kind of film, UV–vis spectroscopy (10, 20, 21), atomic force microscopy (5, 22), and X-ray diffraction or

neutron scattering (23, 24) have been used. These methods can give us the details of the structure, component, and morphology of the formed films, but characteristics such as the wettability of the top layer, which influences the next adsorption, cannot be revealed. Dynamic contact angle (DCA) measurement is a powerful method for studying the surface wettability, roughness, heterogeneity, deformation, and mobility (25, 26). In this contribution, we used the DCA method to investigate the layer-by-layer films fabricated from the oppositely or same charge carried polyelectrolytes to explore the mechanism of the self-assembly more deeply.

EXPERIMENTAL

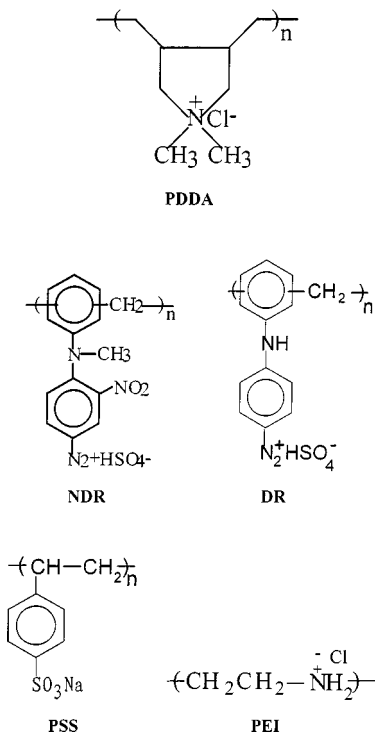
Materials

Diphenylamine-4-diazonium-formaldehyde resin (DR) and 2-nitro-*N*-methyl-4-diazonium-formaldehyde resin (NDR) were synthesized according to the method described elsewhere (27). Poly(sodium-*p*-styrenesulfonate) (PSS) from ACROS (M_w : 10,000 g/mol) and poly(etheleneimine) (PEI) from Sigma (M_w : 50,000 g/mol) were used as received. Poly(diallyldimethylammonium chloride) (PDDA) was synthesized according to Ref. (29), M_n : 60,000 g/mol. Their structural formulas are shown in Scheme 1. The water was distilled and deionized. The vessels used were boiled in the 50% sulfuric acid, washed with distilled water, and then dried.

Film Preparation

The substrate used for the film preparation was freshly cleaved ruby mica (Grade 2), which can dissociate potassium counterions in the water to produce a negatively charged surface with the average charge density of $1/0.48 \text{ nm}^2$. The fabrication was performed in the dark at room temperature. The mica was first immersed in the polycations aqueous solution (2 mg/ml) for 5 min, washed with deionized water, dried, and then dipped into the aqueous solution of PSS (2 mg/ml) for 5 min, followed by rinsing with water and drying in air. Repeating this cycle gave self-organized multilayer films. For the fabrication of DR or NDR, the assembly process was performed by simply immersing the mica into the DR (or NDR) aqueous solution for 5 min and then withdrawing it, followed by rinsing with water and drying.

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SCHEME 1. The structural formula of PDPA, NDR, DR, PSS, and PEI.

Film Characterization

Dynamic contact angle (DCA) measurement. The Wilhelmy plate method was used to measure the contact angles of the mica surface without and with adsorbed polymer, respectively. In each case the mica slide was immersed into and then drawn out of the distilled water with a speed of $150.6 \mu\text{m/s}$.

UV-vis spectrum and atomic force microscopy (AFM). The absorbance of the film was determined on an UV-vis spectrophotometer (Shimadzu 2100). And the morphology of the film on mica was visualized by AFM (Nanoscope IIIA, Digital Instruments, Inc.) in the tapping mode in air at ambient temperature.

RESULTS AND DISCUSSION

Contact Angle Study of the Ultrathin Films

Figure 1 shows a typical graph of contact angle loops by the Wilhelmy method, where the bare mica was immersed into (advancing process) and then drawn out (receding process) of the water. Ordinarily, the advancing line is parallel to the receding line. The process was repeated to obtain the successive second loops. From the buoyancy slopes of the advancing and the receding process, information for the film's surface, such as wettability, roughness, heterogeneity, deformation, and mobility, can be obtained (25, 26). Generally, only the very flat surface can give good buoyancy slopes by the Wilhelmy method. From the graph of the contact angle loop, Eq. [1] is obtained,

$$F = mg + \gamma P \cos \theta - F_b, \quad [1]$$

where the F and F_b represent measured force and buoyancy force, the mg is the force from the substrate's mass, and γ , P , and θ represent the surface tension of the solution (it should be addressed that the surface tension of pure water is constant throughout the experiment), the perimeter of the substrate's underside, and the contact angle, respectively.

The contact angle θ can be calculated according to Eq. [2]

$$\cos \theta = (F - mg + F_b) / \gamma P. \quad [2]$$

The mg can be eliminated by the correction of the baseline. Herein, the θ value, the advancing angle θ_a , receding angle θ_r , and $\Delta\theta (= \theta_a - \theta_r)$, are useful for understanding the wettability of the film. Usually, θ_a represents the state of the surface in air while θ_r represents the state of the surface after hydration, and $\Delta\theta$ represents the film's mobility, reorganization, roughness, etc. As seen in Fig. 1, both the bare mica and that adsorbing a layer of polymer have straight receding and advancing slopes, which shows that the surface is flat. However, the contact angle, which was calculated from the force–depth graph of bare mica and PEI/mica, is obviously different. The bare mica gave an advancing angle (θ_a) of $\sim 20^\circ$ – 30° and a receding angle (θ_r) of 10° – 20° . The small θ_a , θ_r , and $\Delta\theta$ indicates mica has a stiff and

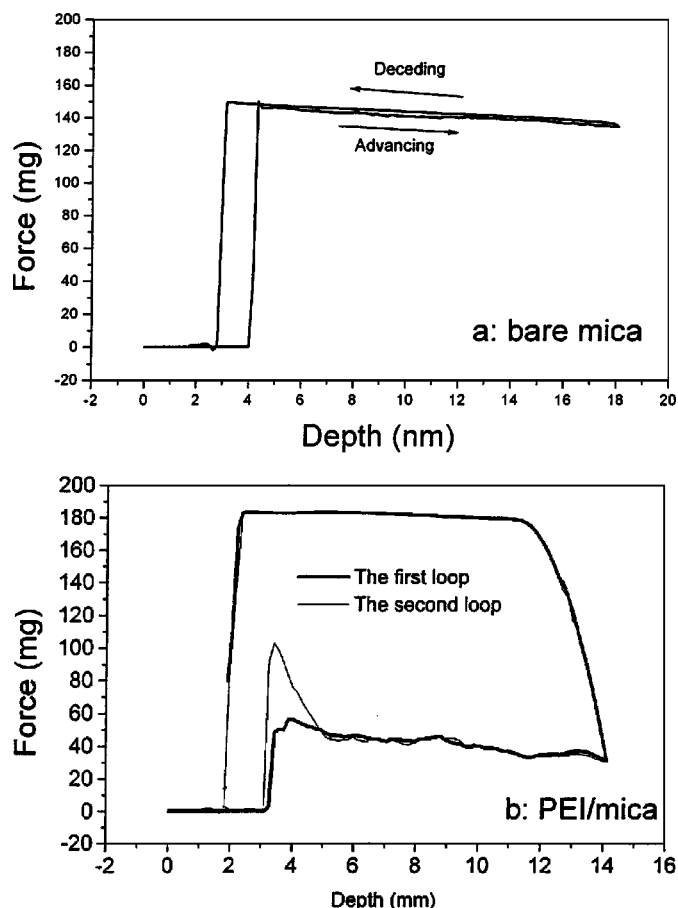


FIG. 1. The graph of contact angle loops measured by the Wilhelmy method: (a) bare mica; (b) PEI/mica.

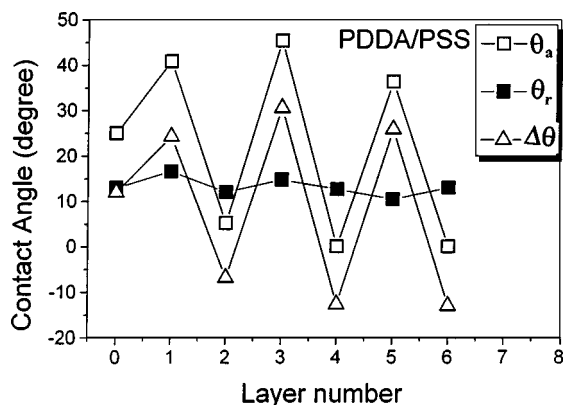


FIG. 2. The relationship of contact angle (θ_a , θ_r) vs number of layers (PDDA/PSS system). Number of layers: 0, bare mica; 1, PDDA; 2, PDDA/PSS; 3, PDDA/PSS/PDDA; 4, PDDA/PSS/PDDA/PSS; and so on.

quite hydrophilic surface. When it adsorbs a layer of polycation, e.g., PEI, the θ_a and θ_r were determined to be 75° and 12° , respectively. The large θ_a and $\Delta\theta$ indicate the surface of PEI-coated mica became soft and less hydrophilic in air, but the small θ_r shows this surface was still quite hydrophilic after being hydrated by water.

The mica/PEI plate was immersed again in a polyanion (PSS) aqueous solution; it adsorbed polyanions easily. The multilayer film can be fabricated via the alternative adsorption of the polycation and polyanion. Herein, we used four different polycations, whose structural formulas are shown in Scheme 1 and PSS as the polyanion to study the formed multilayer films by measuring the contact angle.

PDDA/PSS and PEI/PSS are two conventional self-assembly systems to build up layer-by-layer films reported in several papers (3, 24), and DR/PSS, NDR/PSS's self-assembly multilayer films, have been reported by us (22, 29). The θ_a of the film fluctuates periodically with the layer's alternative adsorption, as shown in Figs. 2–5, which means the layer-by-layer adsorption proceeded well. When the polycation is adsorbed, the θ_a becomes large; while the PSS is absorbed, the θ_a decreases. How-

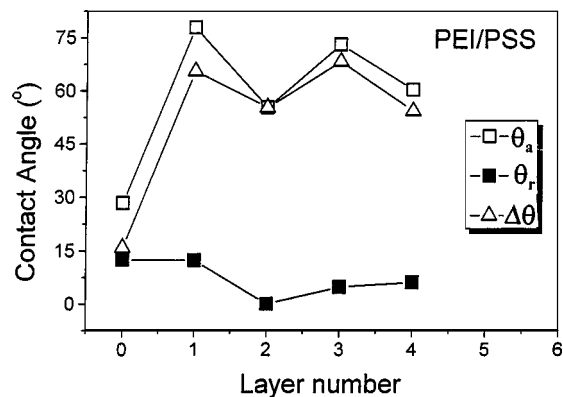


FIG. 3. The relationship of contact angle (θ_a , θ_r) vs number of layers (PEI/PSS system). Number of layers: 0, bare mica; 1, PEI; 2, PEI/PSS; 3, PEI/PSS/PEI; 4, PEI/PSS/PEI/PSS, and so on.

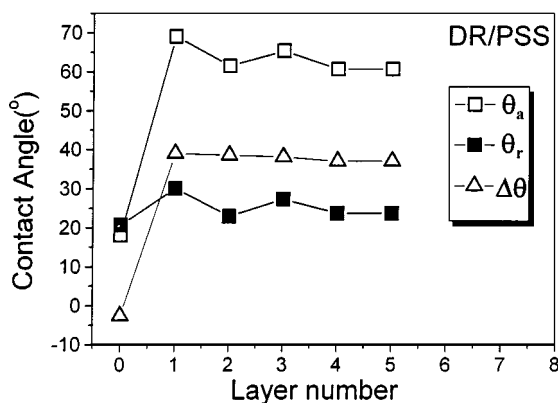


FIG. 4. The relationship of contact angle (θ_a , θ_r) vs number of layers (DR/PSS system). Number of layers: 0, bare mica; 1, DR; 2, DR/PSS; 3, DR/PSS/DR; 4, DR/PSS/DR/PSS, and so on.

ever, the θ_a is different with different polycations. Among them, PDDA gives the most hydrophilic surface (θ_a : $\sim 35^\circ$ – 42° , Fig. 2) and then PEI (θ_a : $\sim 60^\circ$ – 77° , Fig. 3) and DR (θ_a : $\sim 60^\circ$ – 70° , Fig. 4) and then NDR (θ_a : $\sim 68^\circ$ – 80° , Fig. 5). The hydrophilic property of the polycations will influence the next surface of the PSS layer; i.e., for the PDDA/PSS system the PSS layer has the θ_a in 0° – 5° (Fig. 2); for the PEI/PSS system, the PSS layer has the θ_a in 57° – 60° (Fig. 3); the PSS layer in the DR/PSS system has the $\theta_a \sim 60^\circ$ and that in the NDR/PSS system is about 68° . But the θ_r is only a little different since the film is still hydrophilic after hydration.

From Figs. 2–5 we can observe that the various polycation layers exhibit quite different surface behaviors in air but are only a little different after hydration. This is strong evidence that the layer surface is reorganized from in water to in air or vice versa. The hydration can make the ionic groups of the polyelectrolytes stretch into the aqueous phase, resulting in the film being more hydrophilic as shown in Scheme 2a. But when the layer is exposed in air, the soft and hydrophobic moiety of the polycation should divert to the top surface, as shown in Scheme 2b, to meet the minimal surface free energy. The hydrophobic moiety

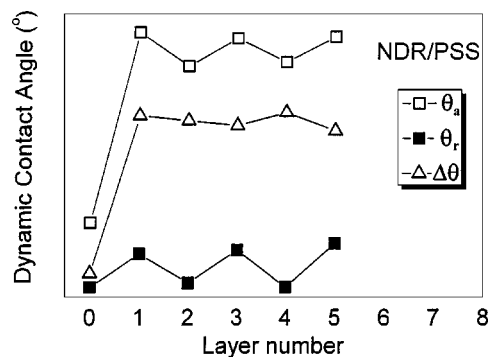
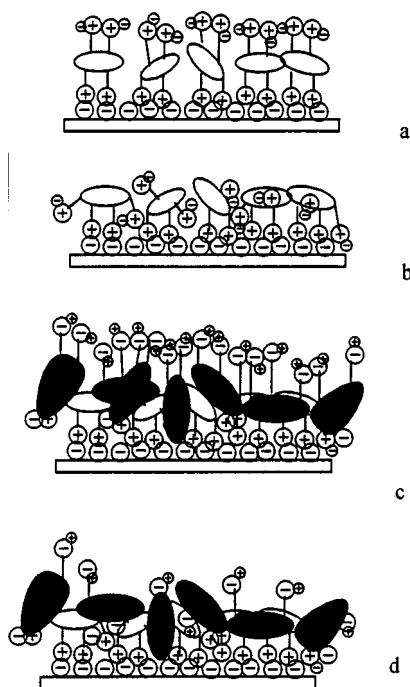


FIG. 5. The relationship of contact angle (θ_a , θ_r) vs number of layers (NDR/PSS system). Number of layers: 0, bare mica; 1, NDR; 2, NDR/PSS; 3, NDR/PSS/NDR; 4, NDR/PSS/NDR/PSS, and so on.



SCHEME 2. The schematic structure of the surface layer of polycation and polycation/polyanion films. (a) A polycation film with a monolayer on mica after hydration with water, from which (film a) the contact angle was determined to be θ_a ; (b) Film a after exposure in air, from which (film b) the contact angle was determined to be θ_r ; (c) Film b after adsorption of a layer of polyanion and hydration with water, from which (film c) the contact angle was determined to be θ_a ; (d) Film c after exposure in air, from which (film d) the contact angle was determined to be θ_r .

is different with various polyelectrolytes. As for PDDA, its hydrophobic ring structure is stiff and difficult to rotate, so its layer is still hydrophilic both in water and in air. DR and NDR have hydrophobic moiety-diphenylamino groups, which makes their films reorganize easily. As a result, the enriched hydrophobic moieties on the surface were obtained in air, which should be responsible for the less hydrophilic surface. PEI is a relatively weak polyelectrolyte, which may explain why the PEI/PSS has a less hydrophilic surface than that of PDDA/PSS.

In addition, the wettability of the polycation layer also greatly influences the subsequent PSS layer since the same PSS layers terminated by different polycations show the different contact angles (Figs. 2–5). This is an evidence that the interpenetration of the adjacent layer is really present. As illustrated in Schemes 2c and 2d, when the PSS is adsorbed, it cannot remain entirely on the top layer, but penetrate into the underlayers. Moreover the underlayers also can move down or upward partly through reorganization; thus, in fact the surface nature is the reflection of two or several layers. When the surface is exposed in air, the reorganization of the charges takes place and makes the surface more hydrophobic as shown in Scheme 2d.

The Layer-by-Layer Films from DR or NDR

As mentioned above, the DR and NDR give a relatively hydrophobic surface. It is also interesting that when we immersed

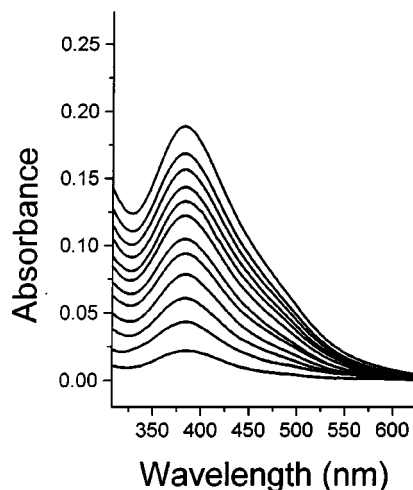


FIG. 6. The UV-vis spectra of NDR films with various number of layers: The number of layers (bottom to top): 2, 4, 6, 8, 10, etc. (Each deposition cycle leads to two-layers growth on two sides of the mica).

the mica, attaching a layer of DR (or NDR) into the DR (or NDR) aqueous solution again, we found that it can re-adsorb itself. With the increase of the immersing–washing–drying cycle, the thickness of the layer-by-layer films increases. Figure 6 shows the UV-vis spectra of NDR films with a different number of layers and Fig. 7 shows the relationship of the absorbance of the DR or NDR film and the number of layers (each deposition cycle leads to two-layers growth on two sides of the mica), which indicates every layer's growth is approximately equal. However, if we simply immersed the mica in the DR or NDR aqueous solution for a longer time, the absorbance of the film increased with immersing time.

To explore the re-adsorption, the DCA method was also used to study the DR or NDR ultrathin film. The graphs of the contact angle loops for the one and three layers are shown in Figs. 8a

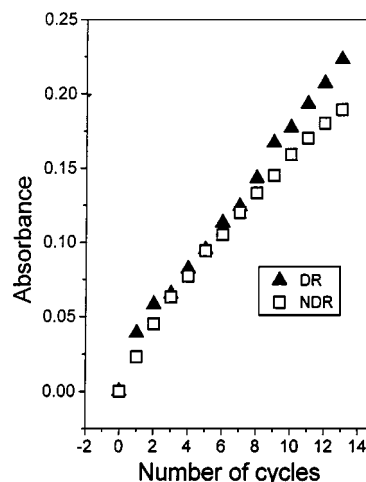


FIG. 7. The relationship of absorbance at 380 nm vs number of layers of DR or NDR.

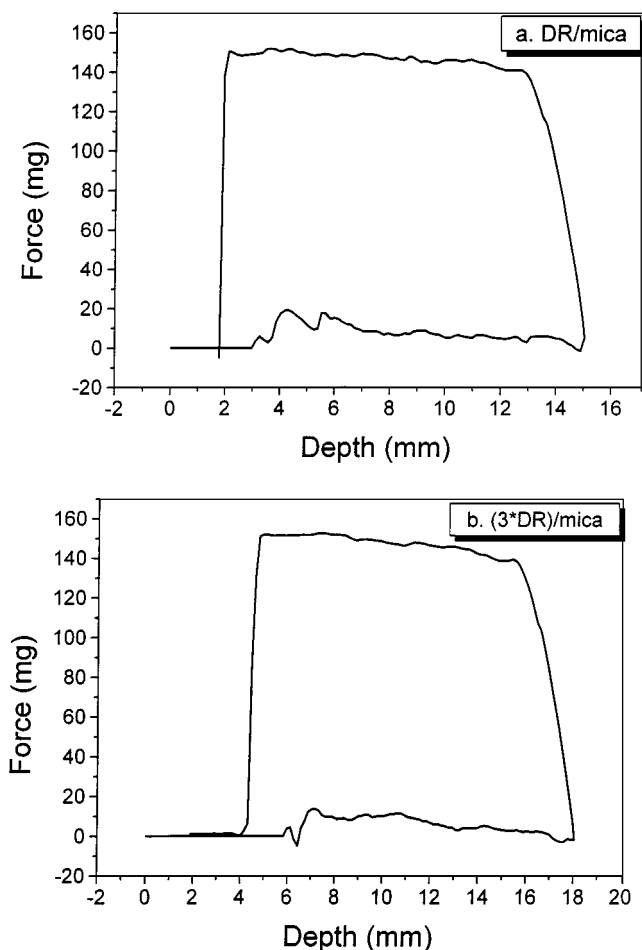


FIG. 8. The graph of the contact angle loops of DR film measured by the Wilhelmy method: (a) DR/mica; (b) (3*DR)/mica.

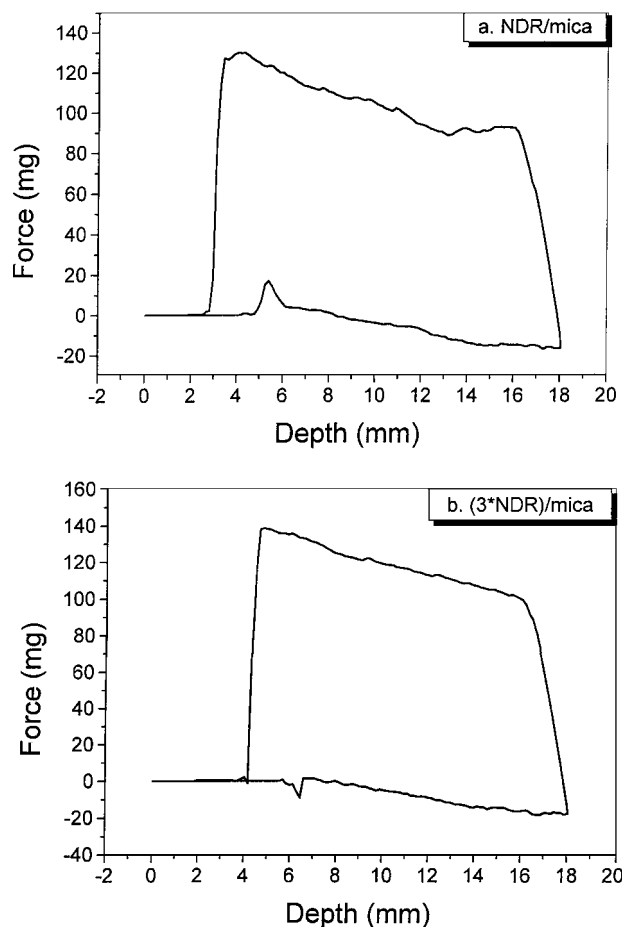


FIG. 9. The graph of the contact angle loops of NDR film measured by the Wilhelmy method: (a) NDR/mica; (b) (3*NDR)/mica.

and 8b for DR film, and in Figs. 9a and 9b for NDR film, respectively. From those we can find that the formed films are quite homogeneous and soft. Figures 10 and 11 show the relationship of the contact angle and number of layers for DR and NDR self-adsorption, respectively. With the growth of the layer, e.g., the film with three layers (Fig. 10b) the surface becomes a little hydrophilic but still maintains a large advancing contact angle (θ_a).

It is worth pointing out that the self-adsorption of the same charge carried polyelectrolytes has been reported by other workers; for example, Decher found that PSS (poly(sodium styrene sulfonate)), can be re-adsorbed on the PSS layer to up to four layers (17), and Helm observed that when two cationic polymers such as PAH (poly(allylamine hydrochloride))/PVP (poly(2-vinylpyridine)), or PAH/PL (poly(lysine)), are used to fabricate multilayer films, an overall thickness of the film increases, at least in the first several layers for both systems (14). They ascribed these phenomena to two possible reasons: (1) when a polyelectrolyte adsorbs onto a substrate, it cannot neutralize all the charges of the underlayer. In the drying step the unneutralized sites will be exposed on the surface after the charge's

reorganization, which leads to the re-adsorption in the next fabrication. (2) The adsorption of the polyelectrolyte on the substrate is an entropy-increasing process, which is favorable to re-adsorption. However, from our experimental results of DR

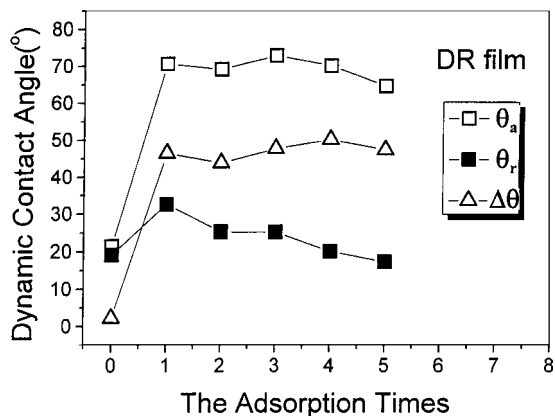


FIG. 10. The relationship of contact angles (θ_a , θ_d) vs number of DR layers. Number of layers: 0, bare mica; 1, DR/mica; 2, (2*DR)/mica; 3, (3*DR)/mica, and so on.

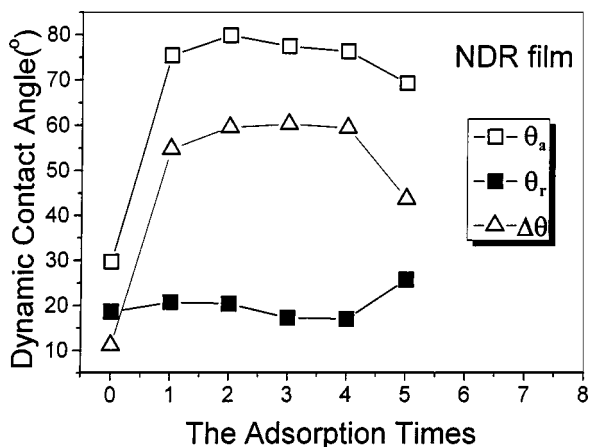


FIG. 11. The relationship of contact angles (θ_a , θ_r) vs number of NDR layers. Number of layers: 0, bare mica; 1, NDR/mica; 2, (2*NDR)/mica; 3, (3*NDR)/mica, and so on.

or NDR self-adsorption, in which the film can be fabricated to at least 13 layers (each side) (Figs. 6 and 7), the explanations mentioned above seem untenable since both the entropy contribution and un-neutralized sites cannot be the driven forces to fabricate the film up to 13 layers (or more). Moreover, compared with the AFM images of bare mica and the first NDR layer (Fig. 12), the surface of bare mica is almost fully occupied by NDR. Therefore, it is reasonable to consider that the hydrophobic interaction should play a key role in which it is responsible for the re-adsorption in DR (or NDR) self-fabrication. DR or NDR has a large hydrophobic moiety, which should produce a strong hydrophobic attraction for self-adsorption. Scheme 3a represents the dried DR or NDR layer film; this surface is rather hydrophobic. When it is immersed into the DR (or NDR) aqueous solution, the interaction between the hydrophobic moieties of DR (or NDR) causes the DR (or NDR) molecules that exist in solution to deposit again on the film surface (Scheme 3b) and makes the surface rather hydrophilic in an aqueous solution. At this time the hydrophobic interaction becomes quite weak, so this re-adsorption is also self-limiting. However, when the surface is blown dry again, the surface becomes hydrophobic again due to the re-organization of the surface charges. It is worth noting that Cochin and Laschewsky (21) recently found that when polycations having different hydrophobic groups with the same polyanion are used to fabricate a layer-by-layer film, the polycation carrying a larger hydrophobic group, will take up more polyanions, and that the hydrophobic interaction between polyelectrolytes plays an important role in self-assembly fabrication.

Another point that should be noted is the re-adsorption takes place only after the film is washed with water and dried, which will be discussed next.

The Influence of the Washing and Drying

When the self-assembly process is used to fabricate the layer-by-layer film, the procedure is composed of two steps: first, the substrate was immersed into the polyelectrolyte aqueous

solution for a given time and then it was withdrawn followed by rinsing with deionized water and air (or nitrogen) drying. The illustrated film in Scheme 2 or 3 shows these two steps.

Usually, the polyelectrolyte molecules can be adsorbed on the surface in different conformations including some loops and coils as shown in Scheme 4a. When the film is washed with water, the loosely attached molecules will be detached and only the well-bound polymer molecules are left (Scheme 4b). In the drying step the surface also reorganizes to meet the changed circumstances from wet to dry (Scheme 4c).

Figures 13a–13d show the DCA profile measured as soon as the substrate was pulled out from the DR solution. The first loop

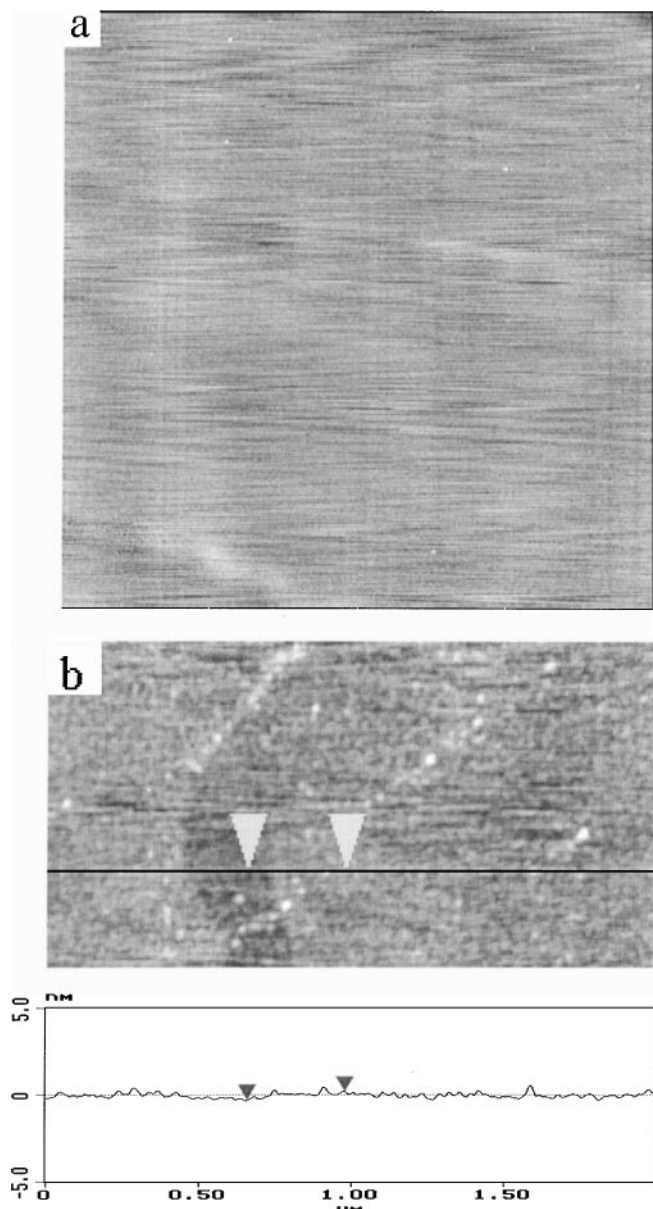
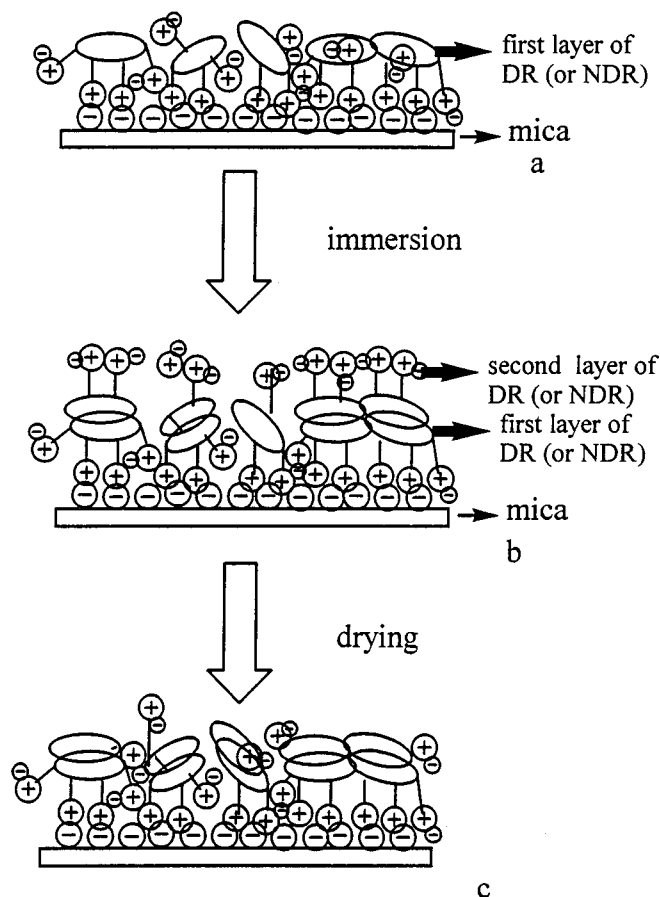


FIG. 12. The film's morphology obtained by AFM in tapping mode: (a) The bare mica; (b) the NDR/mica layer and its roughness profile.



SCHEME 3. The schematic representation of the film formation of DR (or NDR). (a) A polycation (DR or NDR) monolayer on mica after drying in air (film a); (b) Film a after re-adsorption of another layer of DR (or NDR) in water (film b). (c) After drying of film b, some re-organization occurs.

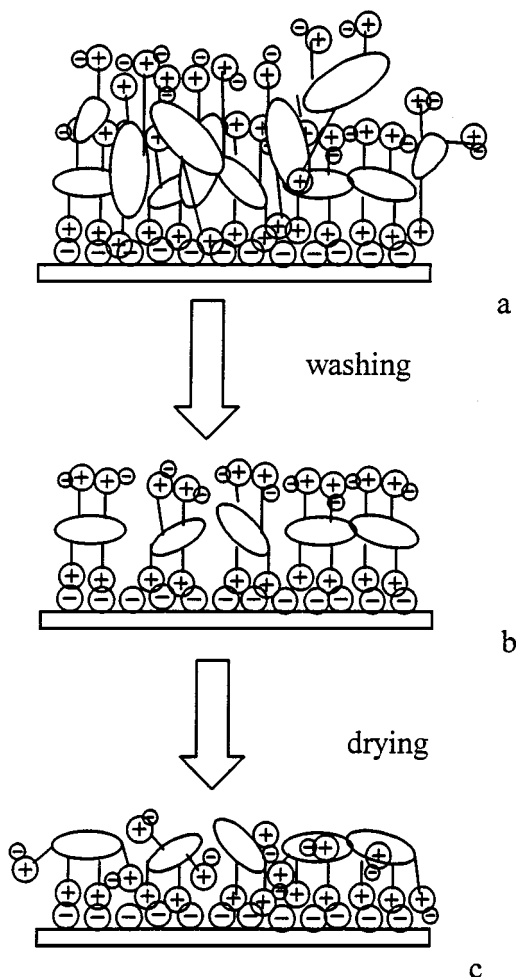
(curve a) gives a seemingly ugly profile, indicating the film is very rough but hydrophilic; the second loop (curve b) shows a relatively flat surface; the third loop (curve c) indicates that from three immersions into the pure water a very flat surface was obtained, and the θ_a is calculated to be 75° . After drying in the dark, the film (curve d) gives a better DCA profile and the θ_a is calculated to be 80° ; i.e., drying makes the film flatter and rather hydrophobic. This means some re-organization of surface charges takes place, which causes the enrichment of the hydrophobic part on the surface through drying. It is favorable to re-adsorption in the next fabrication. This result is in good agreement with Scheme 4.

TABLE 1

Cycle number	1	2	3	4	5	8	12	16
Absorbance ^a	—	—	—	0.044	—	0.06	0.081	0.099
Absorbance ^b	0.039	0.058	0.065	0.082	0.095	0.143	0.207	—

^a Films without drying.

^b Films with drying.



SCHEME 4. The film's surface changes after washing and drying (mica as a substrate). (a) The film just withdrawn from polycation solution. The surface is very rough, (b) after washing with water, the loosely attached polycations were detached, and the film becomes flat, (c) after drying in the air, some re-organization occurs to make the film more hydrophobic.

We simply withdrew the substrate from the DR aqueous solution, then washed it fully, and immersed the wet layer again into the DR solution at once, and so on to finish four deposition cycles. The absorbance of the film then was determined and listed in Table 1. To compare, the absorbance of the film fabricated by the normal procedure (i.e., including a drying step every cycle) was also determined and listed. The absorbance of a 5-layers film from the normal step is almost equal to a 16 layer film fabricated without drying. Therefore, the drying step is necessary for enough re-adsorption. It is reasonable to consider that the hydrophobic attraction contributes greatly to the DR's (or NDR's) self-fabrication. First, the washing step can remove the loosely attached DR (or NDR) molecules, which usually act as a repelling role against re-adsorption of the same charged polyions; i.e., washing weakens the screening effect from the same charges. Second, the drying step is favorable to enhancement of the surface hydrophobic ability via re-organization of

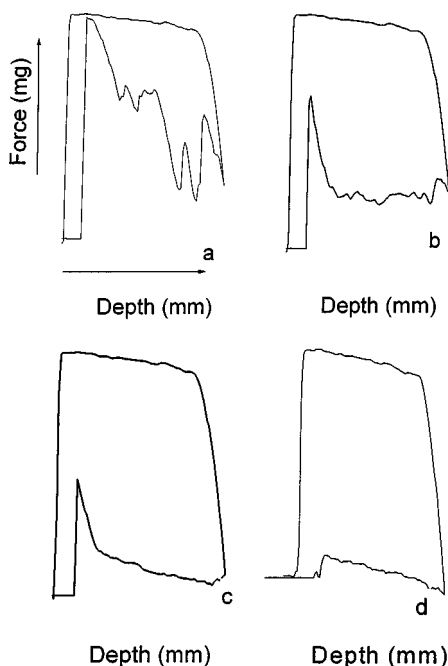


FIG. 13. The graph of dynamic contact angle (DCA) loops measured to determine the role of washing and drying for DR film by the Wilhelmy method. The film was immersed into distilled water when it was just withdrawn from the DR aqueous solution. (a) The first loop; (b) the second loop; (c) the third loop; (d) the loop of dried film c.

its surface charges. Third, the most important reason is that the drying removes the water from the film to make the layers more compact and more difficult to hydrate by water, so the film surface still remains hydrophobic, even in water at the initial time when the adsorption proceeds successfully. Many studies (22, 30) prove that the adsorption of polyelectrolytes on the substrate is very fast, and the saturation of adsorption can be attained in even less than 30 s, which supports the third point. In DR (or NDR) aqueous solution, the hydrophobic attraction causes the DR (or NDR) molecules to re-adsorb on the hydrophobic surface initially.

CONCLUSION

The layer-by-layer films from PDDA/PSS, PEI/PSS, DR/PSS, NDR/PSS, DR itself, and NDR itself were investigated using the dynamic contact angle (DCA) method. In these systems, we found the following:

1. The surface property of the film is greatly dependent on the characteristics of the used polycations. Among them the PDDA gives the most hydrophilic surface and then PEI and DR and then NDR. The various hydrophilic surfaces will also affect the surface nature of the subsequent adsorbed PSS layer. Therefore, we have considered that the re-organization of the components and the adjacent layer interpenetration are present in the multilayered film preparation.

2. The hydrophobic interaction may be the key force responsible for the DR and NDR self-adsorption to form multilayered films.

3. Washing and drying are prerequisites for successful fabrication, especially in the polyelectrolyte itself or those with the same charges.

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